

1) Advanced Nanostructured Materials

P1-01

Polymeric Nanotubes and Nanorods Made from Poly(Styrene alt. Maleic Anhydride) and Poly(pyrrole)

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We recently discovered that it is possible to make nanotubes from alternating copolymers by self-association. An example is poly(styrene-alt-maleic anhydride) (SMA). These polymers consist of hydrophobic styrene groups, alternating with hydrophilic anhydride groups, which hydrolyze in water into two carboxylic groups, which depending on pH, can be both protonated (at low pH), both dissociated (at high pH), or one can be protonated and one dissociated (at neutral pH). At neutral pH an internal H-bond stiffens the molecule. At low and high pH, SMA is flexible and the conformation depends on the chirality of the chain, preventing self-association, whereas for neutral pH the conformation is linear, irregardless of chirality, allowing for a regular association between the chains. This association at pH 7 has been confirmed by dynamic light scattering, Cryo-TEM and SANS. Molecular modeling has shown that the most stable association complex is a nanotube in which 8 SMA chains make up one twist of a helix. The outer diameter of the tube is about 4 nm and the inner diameter 3 nm. The tubes can grow to a length of several microns. The tubes can also associate with themselves, forming sheets, which can stack upon each other. Cryo-TEM and SANS confirm these structures. Filling the nanotubes by monomers and polymerizing them, results in nanorods, which were imaged by AFM.

P1-02

The Role of Substrate Priming in Hydrogen-Bonded Polymer Self-Assembly of Capsules and Films

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Growth of hydrogen-bonded multilayers is affected by substrate shape and charge as well as by deposition conditions of a polycation precursor layer. The growth of strongly-bound poly(N-vinylpyrrolidone)/poly(methacrylic acid)(PVPON/PMAA) and weakly-bound poly(ethylene oxide)/poly(methacrylic acid)(PEO/PMAA) systems is contrasted when these multilayers are deposited onto bare or poly(ethylene imine) (PEI)-treated surfaces of CdCO₃ crystals, colloidal silica particles, or silicon wafers. While in the PVPON/PMAA system robust multilayer deposition occurred on the precursor-treated substrate regardless of the adsorption history of the precursor layer, growth of PEO/PMAA films was critically dependent on the conditions of PEI adsorption. PEO/PMAA films could be grown on CdCO₃ substrates when the PEI precursor was allowed to adsorb at a pH value higher than that used for hydrogen bonding deposition, but PEO/PMAA film growth was inhibited when PEI was deposited at the same pH used for film deposition. This effect is rationalized in terms of the different structure and charge of precursor layers formed through two deposition routes. Two ways to facilitate growth of hydrogen-bonded multilayers onto substrates which carry

unfavorably high negative charge have been suggested: construction of PVPON/PMAA/PEO hydrogen-bonded multilayers and the use of divalent cations as promoters of PMAA binding.

P1-03

Responsive Layers from Heteroarm Star Copolymer

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A grafted layer from poly(2-vinylpyridine)-star-poly(styrene) was prepared and its responsive behavior and phase segregation has been studied using Atomic Force Microscopy, water contact angle measurements, and X-ray Photoelectron Spectroscopy. The heteroarm star copolymer consists of 7 polystyrene and 7 poly(2-vinylpyridine)-arms (PS₇-P2VP₇) emanating from one core made of polymerized divinylbenzene. AFM studies revealed that single molecules of PS₇-P2VP₇ respond to solvent quality by changing their conformation and, therefore, act as spherical mixed polymer brushes. Grafted layers of PS₇-P2VP₇ exhibit very pronounced phase segregation. It was shown that surface composition, morphology, and wettability of such layers reversibly change in response to external stimuli such as solvents of different quality.

P1-04

pH-Sensitive Membranes from Polyelectrolyte Gels

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Cross-linked polymers were used to obtain pH-sensitive membranes. The properties of the membranes were further investigated. Membranes were prepared according to the principles of phase separation in polymer blends. Depending on the composition of the blend, pores' sizes could be changed from hundreds of nanometers to several micrometers. The pore-size of the membranes can be regulated by the change of the pH and ionic strength since they are formed from polyelectrolytes. Membranes could be applied for controllable water transport or selective filtration.

P1-05

Surface Plasmon Resonance Spectroscopy Study of the Adsorption of Surfactants to Electroactive Interfaces

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Well-defined electroactive monolayer films have been prepared by the self-assembly of ferrocenylalkanethiols on gold surfaces. These self-assembled monolayers (SAMs) allow one to electrochemically modulate surface interactions such as adhesion and wetting, as well as induce bulk orientation changes in liquid crystals through potential induced changes in the surface charge density. In the present study a combination of electrochemical characterization and surface plasmon resonance (EC-SPR) was employed to investigate the association of

anionic surfactants to an electroactive self-assembled monolayer as the redox active monolayer is oxidized. SPR was used to quantify the thickness and the refractive index changes resulting from ion pairing between the ferrocenium cation and the counter ion in the solution. We show that the introduction of charges at an electroactive SAMs/solution interface can be used to influence the surface assembly of ionic surfactants and control the molecular organization of surfactants at SAM/solution interfaces.

P1-06

The Use of Self-Patterned Phospholipid Films for Directed Enzyme Lithography

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A novel method based on Langmuir-Blodgett deposition was developed for creating patterned monolayer and bilayer films of phospholipids. Regular stripe patterns with dimensions of few hundreds of nanometers over several square centimetre areas have been generated. Atomic force microscopy (AFM) imaging demonstrated that the stripe patterns are composed of two phospholipids in different phases (solid and fluid). These stripes are easily controlled in terms of lipid composition, surface pressure, and film deposition conditions. In this poster, I will present the mechanism of stripe formation and how the patterned dimensions can be controlled by using lineactants and a combination of different lipids. Preliminary results on selective phospholipid degradation using lipolytic enzymes will be discussed. This work expands the repertoire of template composition and pattern form usable for the fabrication of lipid based surface patterns and nanostructures which could serve to spatially direct enzyme action and enzymatic lithography, and design biomimetic membrane architectures.

P1-07

Fabrication and Study of Responsive Nanoparticles and Colloids

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We report the design and fabrication of smart particles and colloids capable for reversible switching between hydrophilic and hydrophobic states upon external stimuli. Smart nanoparticles are silica nanoparticles with specially designed responsive coating—mixed polymer brush. The mixed brush consists of two unlikely polymers grafted to silica nanoparticles. Two different polymers (A and B) in the mixed brush segregate to avoid unfavorable interactions. The mechanism of phase segregation depends strongly on outside conditions. This adaptive behavior of the mixed polymer brush can be used for engineering surfaces of smart nanoparticles. Polymer A is a water soluble hydrophilic polymer, and the second polymer is a hydrophobic polymer B. In aqueous medium the mixed brush will segregate. Polymer B will segregate to the core, while chains of polymer A will be exposed to the outside. However, in nonpolar organic solvent polymer B will segregate to the core and polymer A will form the outer shell of the particle. In an intermediate case (nonselective solvent for both polymers), the lateral segregation takes place resulting in semi spheres constituted from different polymers. The latter morphology will appear if the particles are introduced into the interface between two immiscible liquids. The goal of this research is to

design smart spherical mixed brushes (nanoparticles) which will change the surface characteristics of different materials due to the responsive behavior of the mixed brushes.

P1-08

Modification of Gold Nanostructures by Using Temperature-Sensitive Core-Shell Microgel as a Template.

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We demonstrate the novel thermo-sensitive hybrid core-shell microgels via in situ synthesis of gold nanoparticles using thermo-sensitive core-shell microgel as a template. The template core-shell microgels whose core were mainly composed of poly(glycidyl methacrylate) (GMA) and shell mainly (or fully) composed of poly(*N*-isopropylacrylamide) (PNIPAM) were synthesized in aqueous medium, and then they were incorporated with functional groups such as thiol, or amino groups. By designing the template structures, we could obtain two types of hybrid microgels. One is hybrid particles with gold nanoparticles localized around the core, and the other is the particles with gold nanoparticles immobilized in the shell. They showed thermo-sensitive properties, especially, in the latter case, the hybrid particles exhibited a reversible color change from red to purple originated from surface plasmon resonance of gold nanoparticles depending on temperature between 25 and 40 degrees. In addition to the thermo-sensitive property, the hybrid particles exhibited unique character of regularly arrangement on solid substrate. The particles obtained by this approach have potential uses for thermo-sensitive applications such as sensor, photonic or electronic devices.

P1-09

Fabrication of Metal Nanostructures Using Self-Assembled Polymer Layers as Templates

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Thin film templates with diverse nanopatterns were designed using the principles of phase separation in polymer blends and block copolymers. The special feature of our approach is the application of low molar mass additives which are easily extracted from the polymer films leaving either nanochannels or nanotrenches. Sputter-deposition and electrochemical deposition were used to fill the templates' cavities with various metals. An additional control over the metal deposition was achieved by an appropriate combination of polar and nonpolar polymer components of the templates.

P1-10

Organization of Gold Nanoparticles on PS-PMMA Block Copolymer Monolayers

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Ordered arrays of metal nanoparticles exhibit unique properties that may lead to important applications in the fields of optics and catalysis. The formation of periodic, ordered structures by block copolymers is well known. Phase separation in block copolymers spread at the air-

water interface offers an interesting route to the preparation of patterned surfaces. For example, polystyrene-*b*-poly(methyl methacrylate) forms ordered arrays of well-defined surface micelles when spread at the air-water interface. These structures are conserved during monolayer transfer to solid substrates by the Langmuir-Blodgett technique. Our current research focuses on the subsequent organization of metallic nanoparticles on these ordered copolymer surfaces. Several strategies are being investigated. One approach involves the organization of amine capped gold particles on sulfonated polystyrene domains of the PS-*b*-PMMA monolayers. Water-soluble gold nanoparticles are prepared by the phase transfer method with two ligands. Gold is reduced by NaBH₄ in the presence of (3-mercaptopropyl)-trimethoxysilane and the particles thus formed are observed to pass into the organic phase. An amine terminated ligand is then introduced and reacts via siloxane binding to produce water-soluble particles. A second strategy involves the direct spreading of polystyrene capped gold particles with PS-PMMA at the air-water interface. The ordered arrays are characterized by AFM and TEM.

P1-11

Composite Films Prepared by Single Wall Carbon Nanotubes Coated Monodisperse Polymeric Microspheres.

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Functionalized monodisperse micron-sized polymeric particles were coated with functionalized single-walled nanotubes (SWCNTs). To coat functionalized SWCNTs on the surfaces of particles, polymeric microspheres (poly (styrene-co-acrylamide)) having the amine group on surfaces were synthesized by dispersion polymerization. SWCNTs were functionalized by chemical oxidation, also. The composite films of SWCNTs coated microspheres were obtained by using hot press at temperature over the T_g of microspheres. The morphology and the properties of the SWCNTs coated microsphere were investigated by a scanning electron microscope, infrared spectroscope, thermal analysis (differential scanning calorimetry, thermogravimetric analysis) and zeta potential analysis. In addition, the conductivity, the hydrophobicity and the morphology of composite films were investigated. The small amount of SWCNTs (the weight of ratio polymer : SWCNTs = 500 : 1) coated on microspheres strongly affects the physical properties of microspheres and composite films.

P1-12

Controlled Alignment of Single-Walled Carbon Nanotubes Using the Langmuir-Blodgett Technique

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The use of single-walled carbon nanotubes (SWNTs) as key building blocks for carbon-based electronics has, in recent years, been demonstrated for a variety of applications such as field-

effect transistors, field-emission materials and sensors. Many of these applications require the integration of SWNTs into ordered macroscopic structures in a controlled way. Despite of extensive efforts, however, it is still a challenge to fabricate large scale, highly organized SWNTs onto solid substrates. Here we describe a method for generating aligned, patterned SWNT structures over large areas using the Langmuir-Blodgett (LB) technique. We synthesized thiophenol-modified SWNTs (SWNT-SHs) through the conventional method based on amidation of oxidized SWNTs. The resulting SWNT-SHs were found to be soluble in organic solvents including chloroform, which allowed the nanotubes to form a stable monolayer at the water/air interface. We found that the compression of SWNT-SHs on a LB trough led to a uniform SWNT-SH film, where SWNT-SHs were aligned parallel to the trough barrier. Moreover the SWNT-SH Langmuir films can be subsequently transferred onto either homogeneous or pre-patterned solid substrates to form aligned SWNT films. Importantly, the electrical conductivity of the resulting SWNT-SH films parallel to the tube axis was found to be ~15 times higher than that perpendicular to the axis, reflecting anisotropic electrical properties due to the uniaxial alignment of individual SWNT bundles.

P1-13

Opportunities Brought by Cationic Fluorinated Surfactants in Tuning the Mesoporous Silica Particle Architecture

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Fluorinated surfactants are special due to the hydrophobic and lipophobic fluorinated chains. These surfactants tend to assemble into aggregates and form novel “intermediate” mesophases more easily than hydrocarbon surfactants. These properties should allow co-assembly with ceramic precursors to create materials with a wider range of pore size and shapes than are available from hydrocarbon surfactants. Fluorinated surfactants also possess processing advantages for organic functionalization and supercritical carbon dioxide processing. We report a comprehensive investigation of the use of cationic fluorinated surfactants as templates for ordered nanoporous silica. A homologous series of cationic fluorinated surfactants with tail lengths between 4 and 12 carbons is synthesized. Using these surfactants, materials are synthesized either in aqueous solution or in water/ethanol solution. Silica powder with pore size as small as 1.6 nm was obtained by using the C4 cationic fluorinated surfactant. This pore size is the smallest among all pore sizes obtained from a surfactant templating process. Silicas with hexagonal pore structure as well as random mesh phase and vesicles were synthesized. The random mesh phase structure and the vesicle structure with mesoporous shells are the first time to be reported. The variety of pore architectures found in this study is much greater than would be found for a homologous series of hydrocarbon surfactants. We relate this structure variety to the known variety of micelle aggregates and mesophases formed by fluorinated surfactants.

P1-14

Synthesis of Fluorocarbon Functionalized Mesoporous Silica Using Fluorinated Surfactant Templates

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Cationic fluorinated surfactants have been successfully used as templates in the synthesis of ordered porous silica materials by our group. This work explores the direct synthesis of organic functionalized silica materials through fluorinated surfactant templating. The general templating mechanism, in which the organic functional groups of the silica precursor are incorporated into the micelle core, is favored by the surfactant and the organic functional group being of like chemical nature. Therefore, in the case of fluorinated surfactant templating, a fluorocarbon functional group may be well aligned within the silica pores. Investigation of direct synthesis of $C_6F_{13}C_2H_4-$, $C_8F_{17}C_2H_4-$ and $C_{10}H_{21}-$ (for comparison) functionalized porous silica materials has been performed. The materials were synthesized using cationic fluorinated surfactants, $C_6F_{13}C_2H_4NC_5H_5Cl$ and $C_8F_{17}C_2H_4NC_5H_5Cl$, and cetyltrimethylammonium bromide ($C_{16}H_{33}N(CH_3)_3Br^-$) as templates.

Fourier transform infrared spectroscopy (FTIR) analysis and TGA confirm the incorporation of the functional groups in the materials after surfactant extraction. Powder X-ray diffraction, transmission electron microscopy (TEM) and nitrogen adsorption analysis are used to characterize the textural properties of the materials obtained from the four different combinations of functional group and surfactant.

P1-15

Self-Assembly of Nanoporous Silica Shapes: Synthesis, Morphogenesis, and Applications

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We study the process of self-assembly of nano(meso)porous silica particles via surfactant templating. Process of formation of the mesoporous silica includes growth of the liquid crystalline template and solidification of this template via polymerization of silica precursor. Material obtained as a result of such synthesis (MCM-41) features highly uniform porosity, a large variety of shapes and their sizes. To control the assembly of the desired shapes, we study their morphogenesis. New conditions of self-assembly are found to form monoshaped nanoporous fibers. Recently suggested Origami-type mechanism for synthesizing a rich family of nanoporous silica shapes (cones, tubes, and hollow helices) is examined. Shape details and their evolution are analyzed by means of XRD, SEM, TEM, AFM, and optical microscopy techniques.

The shapes can possibly serve as templates for various electronic and optical applications. Nanoporous shapes are the prospective hosts for lasing dyes (sealing laser dye molecules inside the silica pores saves them from oxidation and prevents their dimerization). Diffusion from the nanoporous shapes can be used for a control drug release. Another application of mesoporous silica is the coating of optical fibers by uniform low refractive index film with a good adhesion – a possible host for laser dyes or quantum dots.

P1-16

Fabrication and Stabilization of Chain Structures from Fe₃O₄ Nanoparticles in the Magnetic Field.

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A simple method of a magnetically induced formation of chain-like structures from magnetite nanoparticles and a polyelectrolyte in aqueous solution was developed. Massart's coprecipitation method was used for preparing of the aqueous solution of superparamagnetite (Fe₃O₄) nanoparticles stabilized with citric acid. Chain structures were fabricated from the magnetite nanoparticles in the applied magnetic field. The wires were stabilized with polyelectrolyte molecules so that the structures conserve the shape upon dilution, centrifugation, and deposition onto solid substrates. The stabilized magnetic wires were used to fabricate aligned structures by applying external magnetic field. We demonstrate that this strategy could be used for the fabrication of complex hierarchical structures.

P1-17

ESR Study on Nanomolecular Valve Effect of Cu Complex Crystal in Gas Adsorption

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A microporous metal organic solid has a great advantage for designing and construction of the porous framework appropriate for selective adsorption. Li and Kaneko found a remarkably specific adsorption behavior of high reproducibility for CO₂ in Cu complex-assembled microcrystal [Cu(bpy)(BF₄)₂(H₂O)₂(bpy)]_n (bpy = 4,4'-bipyridine) irrespective of no open channels. CO₂ is vertically adsorbed and desorbed at specific pressures at 273 K. Thus, this Cu complex solid is denoted a latent porous copper crystal (LPC). Although the mechanism has not been clear, the mechanism of the nanomolecular valve effect will be presented based on the model structure in another paper in this symposium.

In the present study, the mechanism of the nanomolecular valve effect was examined by the ESR measurement on Cu²⁺ of LPC before and after the gate adsorption of CO₂. The ESR data show the characteristics for monomeric species with axial symmetry before the gate adsorption. The distances between atoms along z-axis are elongated longer than those between atoms in the xy plane because of the Jahn-Teller effect. After the gate adsorption, LPC seems to change to a more isotropic octahedral structure, probably accompanied by the shrinkage of the bond distance along z-axis.

2) Aggregation and Deposition of Colloidal Particles

P2-01

Influence of Anions on Formation of β -FeOOH Particles

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Steel rusts contain β -FeOOH particles in environments containing of Cl such as marine and coastal districts where steels are easily corroded. Besides Cl ions, various anions such as SO_4^{2-} and NO_3^- result from SO_x and NO_x in the atmosphere and SiO_3^{2-} exists in soils, and also PO_4^{3-} is contained in surface treatment agents of steels. In this study, β -FeOOH particles were synthesized by oxidation of FeCl_2 and hydrolysis of FeCl_3 in solutions containing different anions. The resulting particles were characterized by various techniques. The crystallite sizes obtained by XRD steeply decreased with the addition of SO_4^{2-} and HPO_4^{2-} in Fe(II)-oxidation and Fe(III)-hydrolysis. The particle morphology turned from rod to irregular shape on adding SO_4^{2-} and the addition of SiO_3^{2-} increased the particle size. The presence of HPO_4^{2-} also increased the particle size in Fe(II)-oxidation but decreased it in Fe(III)-hydrolysis. The pore size distribution obtained by N_2 adsorption showed that the products with SO_4^{2-} in Fe(II)-oxidation were microporous but those in Fe(III)-hydrolysis were mesoporous.

P2-02

Synthesis of Lanthanide Fluoride Nanoparticles of Varying Shape and Size

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Recent scientific literature demonstrates a growing interest in new methods of nanoparticle synthesis, driven primarily by an ever increasing awareness of the unique properties and technological importance of nanostructured materials. Major issues associated with nanoparticle preparation include the control of particle size and internal structure. We have explored several synthetic routes for the preparation of nanoparticles containing rare earth elements. The fabrication of nanoparticles within reverse microemulsions has been shown to be a convenient route to monodisperse particles of controllable size. Yttrium fluoride nanoparticles of varying crystallinity, shape and size are prepared by precipitation in reverse microemulsions of water in cyclohexane stabilized with polyoxyethylene isooctylphenyl ether. YF_3 particles obtained by the classical microemulsion method are found to be monodisperse amorphous spheres, with controllable diameters between 6 and 50 nm. Furthermore, particles of the same material obtained by a relatively minor variation of this method are found to be monodisperse single crystals of octahedral and triangular shapes. The size of the crystalline particles can be varied between about 25 and 350 nm. The formation of single crystals can be attributed to the slower incorporation of the precipitant into the micelles when introduced in this fashion.

P2-03

Synthesis of Copper (I) Oxide and Metallic Copper Particles in Polyols

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Polyol-mediated synthesis was used for the conversion Cu (II) in to Cu (I) oxide and metallic Cu. Cu acetate (0.001-0.04 mol/l) either in di(ethylene glycol) (DEG) or in 1,2-propane diol (PD) was heated close to the boiling temperature of polyols for different periods of time. The chemical composition, average particle size, and morphology were studied (SEM microscopy, X-ray diffraction and FT- IR spectroscopy) in dependence of the temperature, the polyol used and the concentration of precursor. In DEG copper (I) oxide forms nanorod consisted spheres, that collapse into individual nanorods and they decompose and form irregular shaped metallic Cu particles (30 – 200 nm). In PD copper (I) oxide intermediate forms particles (100-300 nm) composed of small units (10-20 nm). With further heating particles become hollow and Cu particles (100 – 700 nm) are formed. The occurrence of hollow structures in DEG and in PD may indicate that transformation of Cu (I) oxide to Cu involves dissolution of the oxide structure (1). The band at 620 cm^{-1} due to optically active lattice vibrations in oxide was obtained only when the reduction temperature was lower than $195\text{ }^{\circ}\text{C}$ in DEG and $175\text{ }^{\circ}\text{C}$ in PD.

P2-04

Coprecipitation of Composite Colloidal Compounds Copper and Zinc Basic Carbonates
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Previously it was shown that uniform colloidal spheres of mixed metal oxides could be prepared by coprecipitation in solution of metal salts, but the resulting particles were internally inhomogeneous.

This study describes the formation of composite copper/zinc basic carbonates by decomposition of urea in solutions of two metal nitrates in different molar ratios. This system is of particular interest because the copper compound yields spherical and zinc rod-like particles when formed individually under the same conditions. It was found that in the majority of cases by using solutions of both metal salts and ageing them for 90 minutes, the resulting particles are spherical with only a small fraction (1-3%) being zinc base carbonate. Only when zinc nitrate was at least in four fold excess, the obtained solids appear as spherical assemblies formed from nanoribbons. In these instances the selected area diffraction shows that such particles contain up to 80% of the zinc compound.

The particle size increases with the reaction time, most likely by the Ostwald ripening. At still longer aging times (180 minutes) spherical shapes consisting of nanoribbons (zinc base carbonate) are formed.

P2-05

Preparation of the Au Nanoparticles Using NaHCO_3 as a Reducing Agent
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In this paper, the Au nanoparticles were synthesized by polyol process with NaHCO₃ (sodium hydrogen carbonate) as a reducing agent. Utilizing NaHCO₃ in polyol process achieved the low reaction temperature and the short reduction time. Decomposition of NaHCO₃ serves carbonate ions (CO₃²⁻) and a small amount of H₂O which dissolves the carbonate ions in. Carbonate ions increase pH of the mixtures and accelerate the reduction rate of AuCl₄⁻. In our experiments, the effects of the NaHCO₃/Au weight ratio and the PVP concentration on the reduction rate of AuCl₄⁻ and the particle size of the Au nanoparticles were investigated. The NaHCO₃/Au weight ratio was varied to 10, 5, 3, 1 and 1/5. The reduction rate of AuCl₄⁻ was observed by the speeds of the color changes of the mixtures. UV-vis spectra and TEM images indicated that the size of the Au nanoparticles was controlled by the NaHCO₃/Au weight ratio and the PVP concentration.

P2-06

Synthesis of Nanocrystals in Ionic Liquids

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Ionic liquids (ILs) were used in the synthesis of nanostructured CoPt alloys with different compositions and shapes ranging from nanorods, to hyperbranched nanorods and to spherical nanoparticles. The 1-butyl-3-methylimidazolium bis(triflymethyl-sulfonyl) imide ionic liquid, [BMIM][Tf₂N] was employed as the solvent and the reaction was typically conducted at 350 °C under the protection of argon. Platinum acetylacetonate (Pt(acac)₂) and cobalt acetylacetonate (Co(acac)₃) were used as the precursors. The morphology, composition and crystal phase of the resulting CoPt alloy nanocrystals could be controlled by changing the concentration and molar ratio of the platinum and cobalt precursors. The rods synthesized were found having a composition of CoPt using powder X-ray diffraction (PXRD) and energy dispersive X-ray (EDX) spectroscopy. The nanoparticles were found to be CoPt₃. PXRD, EDX, HR-TEM and micro-electron diffraction (ED) were also used in the characterizations of these nanocrystals.

P2-07

Uniform Ag and AgPd Nanoparticles for Ultra-Thin Conductive Metallic Layers

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The aggressive reduction in materials costs and the relentless drive to increase the specific volumetric capacitance are two of the most important trends that characterize multi-layer ceramic capacitor technology. Here we present a novel precipitation process capable of generating highly dispersed Ag and AgPd, core-shell, nanoparticles that can be used to construct ultra-thin (150-200 nm) uniform conductive layers and could pave the way for capacitors with a very high number of electrodes and, therefore, high volume capacitances. Characterization of the particles by Field Emission SEM, X-ray Diffraction, TGA and Laser Diffraction Particle Size Analysis confirms the high purity of the metallic phase and reveals the high degree of uniformity and dispersion of the resulting particles. The precipitation process

developed allows for the deposition of Pd shells representing 2-30 wt%, and is suitable for large scale manufacturing. A novel deposition technique that can be integrated along with these materials in the existing MLCC manufacturing lines with minimal disruption and in a cost effective manner, is also proposed.

P2-08

Multi-Layer Microfluidic Device to Assemble Uniform Colloidal Clusters and Double Emulsions

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We fabricated a novel multi-layer PDMS microfluidic device, which integrates a valve and a Coulter counter, to prepare uniform colloidal assemblies and double emulsions. First, bonding techniques, such as oxygen plasma and a chemical bonding method, and their effects on the bonding strength between two PDMS layers were investigated systematically by monitoring fracture pressure. Second, in this multi-layer device, we developed a novel valve that can stop flow in a microchannel with arbitrary width and depth. The efficiency and the response of the valve are reported. The in-line Coulter counter signals actuation of the valve to prepare controlled-size colloidal assemblies or double emulsions that contain a uniform number of particles or droplets. These advanced structures are expected to have broad applications and significant impact in optical materials and biomaterials.

P2-09

Heteroaggregation Rates and Light Scattering Form Factors of Asymmetric Particle Doublets by Multi-angle Static and Dynamic Light Scattering

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Heteroaggregation denotes aggregation processes in which particle charge and/or size are different. Such phenomena are of greater relevance in applications and natural environments than the analogous processes with identical particles (i.e., homoaggregation). In spite of their relevance, however, heteroaggregation has not been studied much. In this work, the heteroaggregation of two oppositely charged polystyrene latex particles is followed by time-resolved simultaneous static and dynamic light scattering (SSDLS), and from its initial time dependence we can obtain absolute aggregation rates and extract the form factor of the doublets. The heteroaggregation rates are obtained by analyzing the SSDLS data without the need to invoke the optical form factors for the doublets. The experimental form factors are compared with independent calculations based on the T-matrix method and the Rayleigh-Debye-Gans (RDG) approximation. While the RDG approximation is found to be reliable only up to particle diameters of about 250 nm, the superposition T-matrix method is very accurate for all types of doublets investigated, which shows clearly the appropriateness of the T-matrix method to estimate the optical properties of colloidal particles in the micrometer range reliably.

P2-10

Colloid-Colloid and Colloid-Surface Mass Transport Relaxational Kinetics

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We present preliminary results of a Monte Carlo study of mass transport between colloidal particles and colloidal particles and the substrate. Colloidal particles growth has recently taken notorious advances in the literature, but their contact with other particles and to the substrate leading to restructuring has been less studied from a theoretical perspective. We quantify the time scales involved during the restructuring of both particles or between the particle and the substrate. Our study may also shed some light into the ripening of colloids.

P2-11

Measuring Heteroaggregation Rate Constant of Binary Particle Suspension in the Presence of Homoaggregation

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Heteroaggregation between particles of different sizes and properties plays an important role in various applications, such as medicine, ceramics, filtration, flotation, and water purification. In this study, the time-resolved multiangle simultaneous static and dynamic light scattering is used to measure absolute heteroaggregation rate constants in aqueous binary colloidal particles mixtures despite the simultaneous occurrence of homoaggregation. The differences in the form factor of asymmetric dimmers were exploited by using particles of unequal sizes in the range of 100-200 nm, where the Rayleigh-Gans-Debye approximation is accurate. The formation aggregation rate constant for the asymmetric dimmers as a function of the ionic strength was studied up to 300mM.

P2-12

A Coupled Coagulation Model with Arsenic Sorption Kinetics and Equilibrium on Fractal Colloids of Hydrated Ferric Oxide (HFO)

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In recent years, numerous studies have attempted to solve the continuous population balance equations (continuous integro-particle differential equations). To obtain numerical solutions of the continuous population balance equations, extensive computation time and hardware are required. A realistic maximum size used in coagulation modeling would therefore produce an unmanageable number of simultaneous equations to solve. To overcome this computational non-efficiency of the uniform discrete model, various non-uniform discrete schemes have been introduced.

An improved discretized population balance equation (PBE) is proposed in this study. This improved discretized population balance equation has new probability distribution functions for aggregates produced in non-uniform discrete coagulation modeling. In this study, this model was found to be a substantial improvement in terms of numerical accuracy, stability, and computational efficiency over the continuous model. Further, this model was able to simulate the particle aggregation and breakup with fractal dimensions lower than 3. Moreover, comparisons were made using the fractal aggregate collision mechanisms of orthokinetic coagulation with the inclusion of flow induced breakup. This new algorithm makes it possible to solve fractal particle aggregation and breakup problems with high accuracy, perfect mass conservation and exceptional computational efficiency, thus the new model can be used to develop predictive simulation techniques for the coupled coagulation using computational fluid dynamics (CFD) and chemical reaction modeling.

In this study, this improved coagulation model developed was coupled with arsenic sorption equilibrium and kinetics on fractal colloids of hydrous ferric oxide (HFO). The model coupling was achieved by using the colloid stability factor of $W(r_i, r_j)$ and/or particle collision efficiency $a(r_i, r_j)$ as one component of the aggregation rate constant ($k_{agg} = a\beta$) and a main function for coupling coagulation model with chemical reactions such as arsenic sorption. The study reviewed the collision efficiency studies for perikinetic and orthokinetic mechanisms and provided the numerical algorithms to calculate collision efficiency for two different transport mechanisms, depending on two colliding particle geometric sizes and surface potentials or surface charges. Finally, unified model that is coupled coagulation modeling with arsenic sorption kinetics consisting of a sorption diffusion transport model and surface complexation model was developed. Using the coupled model developed in this study, it was possible to predict arsenic sorption (equilibrium and kinetics) and colloid particle collision (surface potential time evolution, coagulation kinetics and particle size distributions) during the arsenic sorption and coagulation, simultaneously.

P2-13

Shape Controlled Growth of Colloid Particles: Numerical Simulation

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In this study we proposed a combinational mechanism of the shape control particle growth. We assume that the aggregation consists of two main processes: deposition, and rearrangement. Numerical simulation analysis was used to study the parameters of the shape maintained growth of the initial particles. The Gaussian distribution function (GDF) was proposed as the main deposition rule for the arriving building blocks. Uniform distribution function (UDF) was suggested as the main mechanism for the rearrangement. Two main parameters: the standard deviation s and the ratio of deposition β have been chosen for the shape maintained growth manipulation. The simulation showed that the combination of parameters $s = 0.5$ and $\beta = 0.2$ gives adequate results up to 20,000 deposited building blocks; this corresponds to the growth of the initial particle twice in volume. Additional rules for further study are proposed.

P2-14

Preparation Methods and Infrared Attenuation Capabilities of Highly Conductive Anisotropic Metallic Particles

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In the present work we have prepared highly conductive anisotropic metallic particles and investigated the ability of their aerosols to scatter and absorb infrared radiation. Copper and silver flakes of high aspect ratio were produced by milling spherical particles of the respective metals. Additional treatments, such as silver coating by conventional galvanic displacement, have been applied to the copper flakes to enhance their dispersion, chemical stability, and attenuating properties. It has been found that during the silver deposition by electro-displacement with metallic copper, silver fibers can form. The formation of these fibers occurs through the growth of the silver clusters at the expense of the copper substrate, their properties being strongly affected by the size and shape of the latter. Mass extinction values for the metallic platelets and fibers were calculated from transmittance measurements acquired by Fourier transform infrared spectroscopy.

P2-15

Control of Micro-Spheroid Silica Structure and Organic Functionalization via a Sol-Gel Method in W/O Emulsion

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A controlled fabrication of silica materials with micro-spheroid type of structure containing a layer of organic functional groups outside the surfaces by using a sol-gel method in W/O emulsion was designed. The presence of Pluronic P123 and surfactants during the acid-catalyzed condensation greatly influenced the final particle morphology.

When Pluronic P123 copolymer was used in the W/O emulsion under the low pH condition, 2 or 3 of water droplets were linearly arranged and inter-condensation of hydrolyzed TEOS molecules occurred. Depending on the surfactants such as non-ionic (Span 80 or AOT), anionic (SDS), cationic (CTAB), used in the aqueous phase, the particle morphology was changed because of the interaction between silica sols and surfactants, including rod-type or egg-type structure. To combine thiol or amine group with the surface of silica particles, 3-mercaptopropyl trimethoxysilane (MPTMS) or 3-aminopropyl trimethoxysilane (APTMS) were used. All samples exhibited characteristic Type II BET isotherms, consistent with non-porous materials. The structure and functionality of these materials were characterized by field-emission scanning electron microscopy, fourier transform infrared spectroscopy, nitrogen adsorption and desorption, optical microscopy, and Energy-dispersive X-ray.

3) General Papers

P3-01

Hydrophobically Modified Polyvinylamine and Poly (ethylene oxide)-Poly (propylene oxide)-Poly (ethylene oxide) Complexes

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Aqueous solution properties of hydrophobically modified polyvinylamine (HMPVAm) and the formation mechanism of HMPVAm / poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) (PEO-PPO-PEO) triblock copolymer complex were studied by dynamic light scattering and fluorescence. The HMPVAm was synthesized by the reaction of polyvinylamine (PVAm) with alkyl bromides. The solution properties of HMPVAm were explained in terms of the balance of hydrophobic interactions and electrostatic repulsion. The influences of the HMPVAm degree of substitution (DS) and solution pH on HMPVAm conformation were significant. Higher DS and pH resulted in a more compact structure. HMPVAm / PEO-PPO-PEO complex solutions were further investigated by dynamic light scattering and fluorescence spectroscopy. Significant changes of light scattering intensity, polymer equivalent size and fluorescence intensity ratio (I_1/I_3) were observed. These results suggested that the HMPVAm and PEO-PPO-PEO complex formation was driven by hydrophobic interactions.

P3-02

Surface modification of EPDM rubber by plasma treatment

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The effect of plasma treatment of thin, solvent cast EPDM films has been investigated by means of AFM, XPS and Surface Energy Measurements. Argon, oxygen and nitrogen plasma was used, and the changes in the surfaces were observed as function of treatment conditions and storage times. A modified surface is normally stable, but some treatment conditions also can lead to unstable surfaces. Surface energies were calculated from advancing contact angle measurements by different methods. Plasma treatment lead to changes in the surface energy from 25 up to 70 mN/m, but the absolute values for the surface energies depended on the method used for calculations.

XPS analyses of the modified surfaces revealed that up to 20wt% oxygen can be easily incorporated in the surfaces, and that variations on the order of 5wt% can be controlled by the plasma conditions. Oxygen was mainly found as hydroxyl groups, but also carbonyl- and carboxyl oxygen functionalities were seen.

AFM measurements revealed different surface structures with the three gases that were used. The surface roughness increased generally with treatment time, and dramatic changes could be observed at longer times. At short times, however, surface energy changes were much faster than the changes in surface structure, showing that plasma treatment conditions can be utilized to tailor both surface energies and surface structure of EPDM rubber.

P3-03

AFM Visualization of Polyelectrolyte Single Molecules under Aqueous Media

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We report on in situ AFM experiments for the visualization of single polyelectrolyte molecules adsorbed on the mica substrate under aqueous environment at different pH and ionic strength. In this experiments we study a weak polyelectrolyte poly(2-vinyl pyridine) when the conformation is affected by the charge density on the polyelectrolyte molecule. The charge density is tuned by change of pH of the aqueous solution and ionic strength (regulated by salt). The experiments allows for the in tact study of the polyelectrolyte conformation introduced by the environment as well dynamic changes of the conformation upon tuned environmental conditions. We compare the conformations obtained in the in situ experiments and the conformations of the molecules in a dry state upon solvent evaporation.

P3-04

Antifreeze Protein: from Interfacial Structure to Antifreeze Effect

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Antifreeze Proteins (AFPs), occurring in some polar animals and plants, are capable of inhibiting ice freezing at subzero temperatures. The antifreeze effect of Antifreeze Proteins on ice nucleation, which was neglected in most studies, was examined based on a “micro-sized ice nucleation” technique in this study. It follows from our experiments antifreeze proteins can inhibit the ice nucleation process by adsorbing onto both the surface of ice nuclei and dust particles, which leads to an increase of the ice nucleation barrier and the desolvation kink kinetics barrier, respectively. It was found that the antifreeze activity of AFPs can be enhanced either by their aggregation at higher concentration or by adding electrolyte into AFPs solutions. This promotion in antifreeze activity is attributed to the rise of surface activity for AFPs aggregates compared to AFPs monomers, and the screening effect of electrolyte to the surface charge of AFPs molecules, respectively. This study enables us to obtain a comprehensive understanding on the antifreeze mechanism of AFPs for the first time.

P3-05

Influence of Ammonia Vapor Post-Treatment on the Porosity of Mesoporous Silica Prepared with Mixed Cationic and Glycoside Surfactant via Nanocasting

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2D-hexagonal structured mesoporous silica samples with variable pore size are synthesized via an acid-catalyzed nanocasting technique using mixtures of cationic and glycoside surfactants, CTAB and n-Octyl β -D-glucopyranoside (C₈G₁). The pore diameter can be tuned by post-treatment of the as-made materials using NH₃ vapor at a mild temperature of 50 °C. Without ammonia treatment, the pore size distribution of silica materials remain almost the same, independent of the ratio of C₈G₁ to CTAB. XRD and TEM indicate only a slight decrease in long-range order. However, the composition of C₈G₁ greatly affects the pore size distribution and degree of long-range order of the materials when the as-made materials are treated by exposing them to vaporized aqueous ammonia. To study the influence of ammonia vapor post-synthesis on the porosity in these samples, two key factors are varied: the amount of silica precursor and the amount of NH₃ vapor. Based on the results, we propose that the

results cannot be explained entirely by a difference in the interaction between silica and cationic or nonionic surfactants at elevated pH. Instead, we propose that the Maillard reaction takes place during ammonia treatment, leading to an increase in pore size but also to a loss of long-range order.

P3-06

ATR-FTIR Study of Adsorption and Structural Arrangement of an Anionic Fluorinated Surfactant at Germanium/Water Interface

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Adsorption of anionic fluorinated surfactants, tetraethylammonium perfluorooctylsulfonate (TEA-FOS) onto hydroxylated germanium from aqueous solution is studied *in situ* using polarized attenuated total reflection FTIR spectroscopy. At pH 6.0, slow and extensive adsorption leading to multilayer formation is observed for a series of bulk solution concentrations spanning from 10% of the critical micelle concentration (1.0 mM) to well above the cmc. Three kinetic stages, with an autoaccelerating last stage, are observed by monitoring the intensity of the fluorocarbon bands. Circular dichroism measurements of CF₂ stretching bands indicate a slight orientation of the fluorocarbon director normal to the surface as adsorption proceeds, but not perfect close-packed layer formation. Further studies indicate that both pH and salt concentrations have significant effect on the adsorption kinetics as well as structural arrangement. With increase of pH, the final surface coverage decrease. However, at even pH ~10, far above the IEP of germanium, the adsorption of anionic surfactant onto negatively-charged surface still can be observed, which indicates that the tetraethylammonium ions mediates the interactions between the surfactant head groups and the surface. The presence of salt increases the initial adsorption rate and change the sequence of steps leading to multilayer formation.

P3-07

Direct Study of Interaction of a Single Nanoparticle with Surfaces by the AFM

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Study of interactions of nanoparticles with various surfaces is of great interest for modern nanotechnology. For the first time, we present a new method to measure such interactions directly. By immobilizing nanosized particles onto the tip of atomic force microscopy (AFM), we are able to carry out direct measurements of the particle interaction with various surfaces. Interactions of ceria nanoparticles and either silica or polyurethane surfaces are demonstrated. The results are applicable to Chemical-Mechanical planarization (CMP). The fundamental issue of interaction between silica nanoparticles and silica plane wafer is addressed by connection of adhesion and long-range forces. We measure both types of forces by means of the AFM in aqueous solutions of various acidities.

P3-08

A Simple and Convenient Method for the Measurement of Electrokinetic Mobility Using a Moving Boundary Method

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Zeta potential is essential for the study of the stability of hydrophobic colloids, and a variety of methods are used for the measurement of the potential. Among them electrophoresis is frequently used. Although many apparatuses for the measurement of the potential are commercially available, most of them are not only expensive but also some of them are not available for small particles in nano-scale. We developed a simple and convenient apparatus for the measurement of electrokinetic mobility using moving boundary method. In this method, a sharp boundary could be created automatically under a flat metal plate or a semi-permeable membrane. This method is not only convenient for the measurement of electrokinetic mobility but also applicable to dispersions of nano-scale particles.

P3-09

A New Approach to Investigate the Deposition of Submicronic Particles by Laser Reflection

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The electrophoretic deposition of micrometer to nanometer size range colloidal particles onto an electrode in aqueous media can result in an ordered array of particles. Such structures are very attractive in a large range of applications: coatings, optical devices, biosensors... In a former investigation, electrodeposition of micronic polystyrene particles on a nickel electrode in a dc electric field was studied. The deposition was observed in situ in a laminar flow cell using optical microscopy. The purpose of the present work is to extend these investigations to the submicronic range of particle size. For that purpose we have developed an experimental setup based on the reflection of a laser beam on the electrode surface. In order to validate the procedure, preliminary experiments were performed using micrometric particles, which could be simultaneously observed with both the regular microscope and the reflection apparatus. A correlation between the two techniques was experimentally and theoretically established, leading to the calibration of the system. This new approach allows in situ investigations of the electrodeposition of nanometric particles (in the range of a few hundred nanometers).

P3-10

Millisecond Time Resolved Neutron Reflection Studies of Electrochemical and Surfactant Systems.

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By synchronizing data collection on a pulsed or chopped neutron source with the application of an external stimulus to a sample it has now become possible to study neutron reflection on time scales from milliseconds to tens of seconds. Recent measurements performed on the

CRISP reflectometer at ISIS and the D17 reflectometer at the ILL have investigated the dynamics of the oxidation and reduction of polyvinylferrocene (PVF), the adsorption and desorption of Sodium dodecylsulfate (SDS) at a gold interface and the switching of a nematic liquid crystal phase. Unlike many other surface sensitive techniques neutron reflection has revealed information about the internal dynamics of PVF at an in-situ solvated interface. The use of isotopic substitution (H_2O/D_2O) allows a unique determination of the solvent and polymer depth profiles and has revealed rate dependent effects in the solvation and desolvation of the polymer film. The continuing development of this neutron reflection technique will add significantly to the information which may be obtained from electrochemical systems as it may be used to probe the relationship between the individual components.

4) Nanoparticles and Colloids in Analysis

P4-01

Modeling and Laboratory Column Study of Transport of Polydisperse Colloids through Saturated Porous Media

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Colloid transport through saturated porous media has been studied by many researchers due to its importance in facilitating the transport of highly adsorbing contaminants in subsurface. However, much of the work has assumed monodisperse colloids. It is well known that natural colloidal particles are normally highly polydisperse. Recent studies have also shown the importance of the advances in understanding the transport of polydisperse colloidal suspensions on the analysis of contaminant transport in streams and pore waters. In this work, we conducted both laboratory column experiments and numerical simulations to study the transport of polydisperse colloids through saturated porous media. Both colloid concentration and particle size distribution of effluent samples collected at the end of the column were measured continuously over time. A polydisperse colloid transport model was developed to simulate the effluent colloid concentration and temporal particle size evolution by considering processes including advection, dispersion, and dynamic colloid filtration. The preliminary experiment results clearly showed a decreasing of particle size over time and a significant higher colloid deposition when background electrolyte concentration was high. The polydisperse colloid transport model was used to simulate both the effluent particle concentration and particle size distribution.

P4-02

Surface Immobilization of Individual Ag Nanoparticles for SERS-based Chem/Bio Sensing

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We report a study on polymer-mediated immobilization of non-aggregated Ag nanoparticles on planar glass substrates and the resultant surface-enhance Raman scattering (SERS) activity

using Rhodamin 6G (Rh6G) as a model molecule. Ag colloidal solution with an average particle diameter of 70 nm was prepared by citrate reduction of AgNO₃ using Lee-Meisel method and subsequent fractionation. Self-assembled polyallylamine hydrochloride (PAH) monolayer was employed as the intermediate polymer layer. We have shown that the coverage density of Ag nanoparticles on the glass substrates correlates with the amount of adsorbed PAH. This parameter can be easily controlled by varying the pH and ionic strength during polymer deposition, with pH 9.0 and 0.25 M NaCl in the buffer solution yielding the highest coverage density. The glass substrates immobilized with non-aggregated SERS-active Ag nanoparticles exhibited in-situ detection sensitivity of Rh6G at sub-ppt level, even under highly acidic or basic conditions. The SERS-active substrates could be regenerated by removing the adsorbed Rh6G in a dilute hydrogen-peroxide solution. The effect of salt addition in the analyte solution on the SERS activity of the glass substrates will be discussed.

5) Nanoparticles, Colloids and Interfaces in Consumer Products

P5-01

Smart Plant Protein Inside Microdevices

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With the discovery of the plant protein forisome, a novel, smart non-living, ATP-independent biological material became available to the designer of smart materials for advanced actuating and sensing. The in vitro studies show that forisomes (1-3 micron wide and 10-30 micron long) can be repeatedly stimulated to contract and expand anisotropically by shifting either the ambient pH or the ambient calcium ion concentration. We probe the forisome's conformation change inside a microfluidic device with the pH modulation. We demonstrate that the surface properties of the channel wall and the flow condition can influence the anisotropic shape change of forisomes, and their actuation kinetics significantly. This study provides insights for multifunctional microvalve fabrication.

P5-02

The Synthesis of Polyvinylamine Microgels and Their Effect on Paper Strength

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Polyvinylamine (PVAm) microgels were synthesized by post-polymerization crosslinking. In this method, linear PVAm aqueous solution was induced to separate phase by adding salt and adjusting pH, followed by the addition of glutaraldehyde which reacted with amine groups on PVAm chains to crosslink the formed polymer aggregations. Three PVAm microgel samples with different mean size were prepared and their contributions to paper strength were tested and the results were compared with those of linear PVAm. Handsheets containing these polymers were made and their dry tensile, wet tensile and internal bond strengths were measured. The results demonstrated that PVAm microgels can improve strength compared to linear PVAm when the polymer dosage is higher than 0.2 wt % based on the weight of dry

pulp. The size of microgels does not have significant effect. Two mechanisms of the better performance of microgels were postulated. Firstly, microgels can achieve higher retention due to their bulk volume; secondly, the deformation of microgels during drying process can fill the voids between rough fibre surfaces to increase the bonding area.

P5-03

Effect of Porosity and Carbazole Concentration on the Reflective Electrochromic Display Prepared by Monodisperse Carbazole-Modified Polymeric Microspheres

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Polycarbazole and its copolymer are the well-known electrochromic materials, which show a dark green color at the applied potential. Reflective electrochromic display (R-ECD) based on polymeric microspheres containing carbazoyl pendants were prepared using the seeded swelling and polymerization method, then synthesized bicarbazole were refluxed with the chloro-functional groups. The porosity and content of carbazole groups were diversified by controlling the amount of toluene and chloropropene in the 2nd monomer mixture, respectively. Response time of R-ECD was considerably affected by the specific surface area of microspheres, and the concentration of carbazole incorporated. The swelling procedure and morphology of polymeric microspheres were monitored utilizing an optical microscopy and SEM, respectively. Reflectance changes were measured by spectrophotometer. Response time and color efficiency of R-ECD were measured by electro-optic spectrometer.

P5-04

Novel Use of Surfactants in Copper Chemical Mechanical Polishing

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Surfactants have been used as one of the components of CMP slurries to mainly stabilize the slurries. However, ionic surfactants can interact with material surfaces and change the property of its surface. In this study, Sodium Dodecyl Sulfate (SDS), one of the conventional anionic surfactants was examined as an inhibiting agent of copper dissolution in chemical mechanical planarization (CMP) slurry. SDS showed superior performance on the inhibition of copper dissolution to Benzotriazole (BTA) at acidic condition. SDS of 1mM effectively shut downed the dissolution of copper film as low as ~0nm/min. and the loss of polishing rate was comparable to that of BTA in the case of typical slurry system of glycine and hydrogen peroxide. According to the contact angle measurement result that can determine the hydrophilicity of material surface, SDS turned the hydrophilic surface of copper film into hydrophobic.

SDS and a positively charged copper-film surface at acidic and neutral pHs (IEP = 9~10) develop electrostatic attraction between them. This electrostatic attraction could introduce a surfactant layer onto the copper-film surface and develop a hydrophobic layer of surfactant.

This hydrophobic layer could protect the copper-film surface from the slurry chemicals that could dissolve the copper surface. And this hydrophobic layer can be removed by the physical forces. So this aspect can maximize the planarization efficiency of copper CMP and minimize the dishing of copper wire.

P5-05

Selective Polysilicon Chemical-Mechanical Planarization (CMP) during Fabrication of Micro-Electro-Mechanical-Systems (MEMS) Devices using Surface-Modified Abrasives

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An important step in micro-electro-mechanical system (MEMS) device fabrication is deposition and etching of few microns thick layers of polysilicon and silicon dioxide. To minimize the processing difficulties in subsequent processes like patterning, deposition and etching, it is desirable to planarize each deposited polysilicon layer using CMP. In one of the several polishing steps during the device fabrication sequence, selective polishing of the polysilicon top layer over the underlying silicon dioxide/nitride layer is required. Hence, a polishing slurry that selectively removes polysilicon over underlying silicon dioxide or silicon nitride is critical to prevent erosion of either silicon dioxide/nitride, which would be detrimental to the subsequent fabrication steps.

Colloidal silica (~50nm) and calcined ceria (~250 nm) based slurries were used to achieve high polysilicon polish rates (250-500 nm/min) and high selectivity of polysilicon over silicon dioxide and silicon nitride (> 75:1). The surface characteristics of the abrasive and wafer surface were modified in the presence of several additives. The additive role in the suppression of silicon dioxide and silicon nitride removal rates by adsorption to the abrasive and wafer surface was confirmed through Fourier transform infra- red (FTIR) spectroscopy and zeta potential measurements.

P5-06

Role of Complexing/Chelating Agents in Copper CMP Slurries

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Typically copper CMP slurries are composed of an oxidizer, the most preferred one being hydrogen peroxide (H₂O₂), a corrosion inhibitor like benzotriazole (BTA), a complexing/chelating agent and other additives along with abrasives like silica or alumina. Glycine, citric acid, ethylene diamine, ethylene diamine tetra acetic acid are some of the many complexing/chelating agents that have been investigated in Cu CMP slurries. However, there has been no definitive elucidation of the role of the molecular structure of the complexing agents - different functional groups (eg: -NH₂ vs. -COOH), their relative positions, the length of the carbon chain, etc., - in interacting with copper surface and controlling the material removal rates. In this study, several complexing agents containing amine and/or carboxyl groups (acetic acid, succinic acid, ethylene diamine, glycine, alanine, amino butyric acid and

others) have been studied to understand better the role of the molecular structure in determining copper removal rates. The results are consistent with the known activity of –COOH groups at acidic conditions and that of –NH₂ groups in an alkaline environment. In comparison with glycine, it was also observed that an increase in the carbon chain length increased the removal rates at acidic pH values and decreased the removal rates at alkaline pH values. Also, Cu removal rates decreased with an increase in the distance between the –NH₂ and –COOH groups in an amino acid at all pH values except at 4.

P5-07

Influence of Particle Surface Charge with Charged Oxidizing Agents for Cu CMP

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Hydrogen peroxide has played a vital role in many of the copper CMP systems involved in the manufacturing of IC chips. Recent studies on the use of hydrogen peroxide have suggested mechanisms for the formation of hydroxyl radicals (*OH) as the key component in modifying the copper surface. These hydroxyl radicals are highly reactive intermediates bearing no formal charge leading to very little or no interaction among the charged abrasive particles within a CMP slurry.

Substituting potassium persulfate for hydrogen peroxide in a traditional system has shown promise in the removal and planarization of the overburden copper. Knowledge of potassium persulfate suggests a mechanism, through single-electron transfer and the presence of water, in which there is a production of sulfate radical anions and hydroxyl radicals. These sulfate radical anions carry a formal charge of -1 allowing for interaction among charged abrasive species.

This presentation will demonstrate how the charge of a particle will influence the removal and planarization of copper using anionic oxidizing agents. The particles being studied will possess no surface charge, negative surface charge or positive surface charge within the aqueous slurry.

P5-08

Effect of total surface area of solids on material removal rate in metal polishing

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The properties of abrasive particles play a significant role in chemical mechanical planarization (CMP) of metal films. The effect of particle size (silica) on the material removal rates of copper and tantalum in hydrogen peroxide based slurries containing glycine as a complexing agent was investigated earlier^a. It was shown that the total surface area of the solids in the slurry controlled the material removal rates for both Cu and Ta. The present work extends these studies to other complexing agents: citric acid, maleic acid and acetic acid.

P5-09

Role of Oxalic acid in Slurry for Copper CMP

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Copper (Cu) disks were polished using oxalic acid and H₂O₂, with and without abrasives (3 wt % colloidal silica – 50 nm), at different values of the solution pH. Cu polish rates with and without abrasives were similar, indicating that oxalic acid is an effective complexing agent in abrasive-free slurries. At pH ~ 1.5, dissolution rates of Cu in slurry containing oxalic acid and H₂O₂ were low and the rates increase with an increase in the pH till pH = 3.0. A similar trend was observed with the polish rates of Cu. At pH = 3.0, when the concentration of H₂O₂ was increased from 0 wt % to 5 wt % in the slurry, the dissolution rates increased, becoming almost constant thereafter till 8 wt % H₂O₂ and then decrease with a continued increase in the H₂O₂ concentration. Electrochemical and UV/Visible spectroscopic measurements were performed in order to understand the observed trends of Cu polish rates and formation of Cu-oxalic acid complex.

6) Nanoparticles, Colloids, and Interfaces in Medical/Biomedical Diagnostic Products

P6-01

Controlled Release of Plasmid DNA from Gold Nanorods Irradiated by Pulsed Near-Infrared Light

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Gold nanorods (NRs) are rod-like nanoparticles that have unique optical properties depending on their shape. In order to use NRs for biochemical applications, we have first partially modified them with phosphatidylcholine (PC). Partial modification of NRs with PC has been successful by extraction with chloroform containing PC. The resultant PC-modified NRs (PC-NRs) could form complexes with plasmid DNA by electrostatic interactions, denoted as PC-NR/DNA. Pulsed laser irradiation of NRs induces shape changes into spherical nanoparticles. Irradiation of pulsed 1064-nm laser light (250 mJ/pulse, 2 min) to PC-NR/DNA complexes induced shape changes of PC-NRs and at the same time plasmid DNA were released from the complexes as confirmed from gel electrophoresis. Thus, it is clear that the shape changes of PC-NRs trigger the release of DNA from the complexes. It was also found that the plasmid DNA was released without any damage by laser irradiation. Thus, the near-IR laser irradiation onto the PC-NR/DNA complexes has realized the selective release of the plasmid DNA without appreciable structural changes.

P6-02

Preparation and Characterization of Genistein-Modified PLGA Nanocapsules by Introducing the Cationic Moiety

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Nanocapsules, which formulated from the biodegradable polymers such as poly(D,L-lactide-co-glycoide) (PLGA), poly(D,L-lactide) (PLA), are being extensively investigated as drug release vehicle, or specific carriers for gene delivery. Genistein, extracted from soybeans, is one of the good anti-oxidant agents, therefore, it was chosen a model drug in this study. A cationic moiety, amine structure, was incorporated to the PLGA to capsule the genistein more efficiently. The modified PLGA-genistein nanocapsules were prepared by using a emulsion-evaporation method. At first, the modified PLGA and genistein in acetone solvent were poured into the Tween 60 aqueous solution with a mechanical stirring. Encapsulation of genistein was achieved by means of the ionic interaction between anionic hydroxyl groups of genistein and cationic amine groups of modified PLGA in the micelles. The content of genistein in nanocapsules and antioxidant activity of capsules were examined utilizing an high performance liquid chromatograph (HPLC) and 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging method, respectively. Depending on the concentration of cationic moiety in the modified PLGA, the *in vitro* release profiles of genistein was also investigated.

P6-03

Patterns of the Salt Effects on Protein-Protein Interactions and Their Implications for Protein Crystallization

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Proteins have a typical size of few nanometers, and so are in the lower range of the colloidal domain. In order to map out the main patterns of protein-protein interactions, the second osmotic virial coefficient (B_{22}) has been measured using self interaction chromatography (SIC) for seven different proteins (ovalbumin, ribonuclease A, myoglobin, α -lactalbumin, BSA, catalase, cytochrome C) under different conditions of salt and pH. At low salt concentrations the protein interactions can be either attractive or repulsive. At higher salt concentrations, when electrostatic interactions are completely screened, the trends depend of the type of salt. In sodium chloride, for all the proteins studied the B_{22} remains unaffected, whereas in ammonium sulfate B_{22} drops steeply at different salt concentrations for each protein. These last trends emphasize the importance of non-DLVO forces on protein interactions and are mainly interpreted in terms of an hydration effect.

7) Nanoparticles, Colloids, and Interfaces in Pharmaceuticals and Drug Delivery Applications

P7-01

Thermodynamic Study of the Effects of Procaine on Phospholipid Monolayers

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The influence of the local anesthetic procaine (PR) on 1,2 – dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) monolayers was investigated at the air/water interface by Langmuir technique. Compression isotherms were investigated as function of concentrations of procaine hydrochloride in aqueous solutions in the range from 10^{-6} to 10^{-2} M. The amount of PR penetrating into the DPPC monolayers was derived from the surface pressure increase with increasing procaine concentrations recorded at constant molecular area of DPPC by using the Gibbs' adsorption equation adapted to interfacial penetration phenomena. The findings show that the presence of DPPC monolayers produces an enhanced adsorption of PR at the air/water interface. At the monolayer collapse an exclusion of PR molecules from the DPPC monolayers is evidenced by atomic force microscope observations on Langmuir-Blodgett films transferred on solid substrates. The pressure dependence of the penetration of the local anesthetic procaine into the phospholipid monolayers may be of relevance in the phenomenon of pressure reversal in anesthesia.

8) Nanoparticles, Colloids, and Interfaces in the Environment

P8-01

Colloid Retention and Transport in Porous Media with Mixed Wettability

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Migration of colloids can facilitate transport of bacteria, virus, metal, and radionuclide in the subsurface environment. In this study, saturated and unsaturated column experiments were conducted to examine the behavior of latex particles with diameter of 19 nm in 300 to 355 μm sand with mixed wettability using buffer solution with a constant ionic strength of 100 mM and constant pH of 7.5. Batch experiments were conducted with hydrophilic sand, hydrophobic sand and the mixture of them. The initial colloid concentrations were 1, 2, 5, 10, 20, 50 and 100 mg/L. Air was completely eliminated from all tubes in order to avoid colloid attachment at the air-water interface and examine sorption of colloids onto solid surfaces only. Results from this study suggested that there was significant retardation of latex particles breakthrough in the presence of hydrophobic sand and it became more significant as the fraction of hydrophobic sand increased. Strong partitioning of colloids onto the hydrophobic surface was likely the main mechanism contributing to the delay. Colloids behaved differently between homogeneous hydrophilic media and mixed media under unsaturated conditions, which was attributed to the different water flow paths.

P8-02

Design Criteria for Laboratory Reactors Used to Evaluate the Deposition of Colloidal Particulates on the Surface of Steady State Aerobic Biological Films of Any Thickness

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Generally, a substantial effort is put forth in the design of a bench-scale experimental apparatus when evaluating fixed-film biological wastewater treatment systems. During kinetic investigations, steady state conditions with respect to effluent particle concentration

are desirable because they allow for the most simplistic model development and verification. The steady state conditions in an ideal biofilm reactor include evenly distributed biofilm with constant values of film thickness, pH, colloidal particulate concentration remaining in the effluent, DO level, and negligible suspended growth. Realistically, these variables will fluctuate slightly. However, the laboratory reactor must minimize this variation in order to obtain a quasi-steady state with respect to effluent particle concentration. There is a paucity of information in the literature detailing the design criteria for such a reactor. This presentation details the experimental setup including: nutrient solutions necessary for film development and maintenance, commercially available colloids (organic and inorganic), construction material, motor integration, and sampling. Additionally, appropriate inoculation sources as they pertain to experimental objectives are addressed. A presentation of recent research that demonstrates particle removal by aerobic biological films is governed by a physical surface dependent process, namely bioflocculation, indicates colloid analyses can be conducted on films of any thickness.

P8-03

Kinetic Study of Cell Proliferation of *Saccharomyces cerevisiae* Strains by Sedimentation/Steric Field Flow Fractionation in Situ

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The Sedimentation/Steric Field Flow Fractionation (Sd/StFFF) technique is applied to the kinetic study of cells proliferation of *Saccharomyces cerevisiae* (*S. cerevisiae*) strains. The size distribution and the mass ratio of the yeast cells were determined as a function of the time from the preparation of the yeast sample dispersion in the culture medium. The results were combined with the growth of the yeast cells and their life cycle and compared with those obtained by scanning electron microscopy (SEM) and those found in the literature. Useful conclusions concerning the budding and the fission of these yeast cells were also extracted.

P8-04

Diffusion Coefficients and Partition Coefficients of SO₂ in Water – Air Interface at Different pH Values in the Presence or Absence of Surfactants.

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The physical and chemical phenomena controlling the exchange of gas pollutants between atmospheric and water environment are of great significant in environmental chemistry. Research in this area requires working at scales far smaller than those normally associated with the bulk processes on either side of interface, and requires new experimental and theoretical approaches.

In this work the relatively new technique of reversed flow gas chromatography (RF-GC) has been applied for measuring the diffusion coefficients of one of the most common pollutant, SO₂, in water at different pH. Also their partition coefficients in water-air interface were

calculated giving information not only on phase equilibria but also on interface transport across the air – water boundaries.

Finally the effect of surfactants (FL-70 and Triton) on the transfer of SO₂ into water was studied.

P8-05

Influence of dissolved organic matter and pH on the transport of *Cryptosporidium parvum* oocysts in a geochemically heterogeneous saturated porous medium

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Dissolved organic matter (DOM) may affect the attachment of *Cryptosporidium parvum* oocysts (a pathogenic protozoan pathogen) in aquifer sediments by altering the surface characteristics of the oocysts and the grains. To test the effect of DOM on oocyst transport in geochemically heterogeneous porous media, we measured removal of oocysts in flow-through sand columns in the presence of a well-characterized fulvic acid (FA) from the Florida Everglades (0 to 20 mg L⁻¹) under low pH (pH 5.6-5.8) and ionic strength (10⁻⁴ M) conditions. The columns were packed with a mixture of quartz sand (96%) and ferric oxyhydroxide-coated quartz sand (4%). Deposition of oocysts within the sand columns decreased with increasing FA concentration. Collision efficiencies (α) decreased from 0.25 to 0.12 as the FA concentration increased. To test the effect of pH on oocyst transport in similar geochemically heterogeneous porous media, a second set of flow-through sand columns were conducted over a pH range of 5.7 to 10.0 at low ionic strength (10⁻⁴ M NaCl). Results of these experiments demonstrated that the magnitude of oocysts breakthrough was sensitive to pH; the increase in pH from 5.7 to 10.0 decreased a by 50 %.

9) Nanoparticles, Colloids, and Interfaces in Advanced Catalytic Materials

P9-01

Characterization of Ni-Zn/TiO₂ nanoparticles synthesized by liquid phase selective-deposition method

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Liquid phase reduction method is among various methods to synthesize nanometer-size metallic particles as catalyst. It has been reported that nickel and nickel-zinc nanoparticles synthesized by liquid-phase reduction method had amorphous-like structure with a diameter from 5 to 10 nm. Additionally, the catalytic activity was promoted for 1-octene hydrogenation by adding Zn to Ni nanoparticles. However, unsupported nanoparticles lost their high catalytic activity due to aggregation. In order to solve this problem, we have been reported that Ni nanoparticles were selectively deposited onto support materials such as TiO₂. In the present study, the addition of Zn proved to decrease the nanoparticles size, leading to the

increase in the total area of catalytically active Ni surface. In addition, nanoparticles were highly stabilized by the deposition on TiO₂, so that the catalytic activity of Zn-added TiO₂-supported Ni nanoparticles (Ni-Zn/TiO₂) in the 1-octene hydrogenation was ca. 10 times higher than that of unsupported Ni nanoparticles.

10) Nanostructures for Quantum Device Development

P10-01

Material Properties Optimization for Solid State Quantum Computing

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Different approaches in quantifying environmentally-induced decoherence are considered. We identify a measure of decoherence, derived from the density matrix of the system of interest, that quantifies the environmentally induced error, i.e., deviation from the ideal isolated-system dynamics. This measure can be shown to have several features useful for optimization of a particular quantum computer design which includes selection of the suitable materials and regimes for coherent control. As a representative example, decoherence of an electron in double quantum dot due to the interaction with acoustic phonons is considered for different experimentally accessible materials.

P10-02

Quantum Dynamics of Electron in a Cycle of Coupled Quantum Dots

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We derive the set of dynamical equations describing quantum evolution of electron in the array of semiconductor quantum dots forming circle. In the limit of weak decoherence the asymptotically exact analytical solution of these equations is obtained. The effect of decoherence on particle dynamics at stronger decoherence rates obtained numerically is also presented. Results show non-trivial dependence of hitting and mixing times upon the decoherence rate.

P10-03

Loss of Coherence in a Qubit Subject to Time-Dependent Gates

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We present the results of the investigation on decoherence processes in qubit systems manipulated by external gates. Different types of time-dependence for the gate functions are considered. We utilize Magnus unitarity-preserving expansion to formulate the approximation

for the evolution operator suitable to handle essentially time-dependent gates. Estimates to decoherence of a qubit controlled by the external rotating wave are obtained.

P10-04

Decoherence and Loss of Entanglement

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We review our recent work establishing by an explicit many-body calculation for an open quantum-mechanical system of two qubits subject to independent noise modeled by bosonic baths, a new connection between two important issues in the studies of entanglement and decoherence. We demonstrate that the decay of entanglement is governed by the product of the suppression factors describing decoherence of the subsystems (qubits). This result is the first detailed model calculation proving an important and intuitively natural physical property that separated open quantum systems can evolve coherently, quantum mechanically on time scales larger than the times for which they remain entangled.

Our result also suggests avenues for future work. Specifically, for multiqubit systems, it is expected that similar arguments should apply “by induction.” This will stimulate research to develop appropriate quantitative measures of entanglement, and attempts to quantify entanglement and decoherence in a unified way.

P10-05

Qubit Decoherence due to Interaction with Non-Ideal Phonon Bath.

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Most recent studies of non-markovian evolution of a two-level quantum system due to interaction with a bath are based on a spin-boson model, where a thermal bath is represented by a set of non-interacting oscillators. However, in realistic systems the later assumption of non-interacting modes of a bath is not valid. We study how internal dynamics of a phonon bath due to phonon-phonon interactions and isotope scattering affects irreversible evolution of a qubit.

P10-06

Monte Carlo Simulation of Spin-polarized Injection in a Schottky Diode

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Spin-polarized injection in an Fe(100)/GaAs(100) Schottky diode is investigated by Monte Carlo simulation approach. Scattering mechanisms of both intra-valley and inter-valley are considered. Spin dynamics in the G and L valleys are taken into account in the model. The

simulation shows that the upper (L) valleys have significant influence to spin transport close to the Schottky barrier. The simulation results are in good agreement with experimental data.

P10-07

RKKY Interaction in 1D Electron Systems

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The indirect interaction between localized spins in 1D electron systems is considered within the frameworks of Luttinger model. It is shown that interaction between conduction electrons serving as carriers of indirect interaction between localized spins plays a significant role.

11) Preparation and Applications of Soft Colloids

P11-01

Thermodynamic Approach on Specific Interactions in Mixed Lipid and Carotenoid Monolayers

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Mixed lipid and carotenoid monolayers spread at the air/water interface, namely (1) egg lecithin : β -cryptoxanthin; (2) egg lecithin : β -cryptoxanthin palmitate; (3) egg lecithin : zeaxanthin monopalmitate; (4) distearoyl lecithin : zeaxanthin; (5) distearoyl lecithin : astaxanthin; and (6) distearoyl digalactosyl glycerol : astaxanthin have been investigated. The curves of surface collapse pressure versus monolayer composition are discussed in terms of surface mixture thermodynamics. It has been found that the system (1) presents a perfect behaviour throughout the entire range of composition, while systems (2) and (3) can be satisfactorily described by the regular solution theory. For systems (4) - (6) a new approximation is proposed, considering the formation of supramolecular associations in monolayers. The stability constants of the supramolecular complexes in monolayers are calculated and correlated to the specific interactions that can occur in these mixed monolayers in substantial agreement with the molecular structures of the investigated biocompounds.

P11-02

Formation of Nanolattices within Phase Segregated Micelles

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The growth of polymer nano-lattices in novel microemulsions has been studied. The systems used exploited the natural incompatibility of fluorocarbon and hydrocarbon materials to drive local phase segregation inside the microemulsion droplets. This was achieved by using a matrix of systems comprising of fluorocarbon and hydrocarbon surfactants and monomers.

Both thermal and UV initiated polymerizations have been carried out and the effect this has on the final lattices studied. These polymerizations have been followed via ^1H NMR and SANS/SAXS and the final products imaged via TEM. Results will be reviewed and future prospects presented.

P11-03

Thermal and Rheological Properties of Carbon nanotube-in-oil Dispersions

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Prior work on asymmetric thermally conducting nanoparticles in dispersions with low thermal conductivity liquids has shown that it is possible to tailor fluids with higher thermal conductivities than the base fluid at modest volume fractions of nanoparticles. Stable and reproducible nanotubes dispersions require careful control of the dispersant chemistry as well as an understanding of their response to shear and temperature changes. This paper addresses the effects of dispersant concentration, energy per unit volume for dispersion, and nanoparticle loading on thermal conductivity and steady shear viscosity of nanotube in oil nanofluids. The thermal conductivities and viscosities of these dispersion correlate to each other, and vary with the size of large scale agglomerates, or clustered nanoparticles, in the fluids. Fluids with large scale agglomerates have high thermal conductivities. Dispersion energy such as sonication can decrease agglomerate size, but also breaks the nanotubes, decreasing both the thermal conductivity and viscosity of nanofluids. Developing high thermal conductivity nanoparticle dispersions may require a balance between the high thermal conductivity of agglomerate structures and the high viscosity of these fluids.

P11-04

Selective Aggregation of Morin in Different TritonX-100 micelles

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Morin (3,2',4',5,7-pentahydroxyflavone) is one of the effective antioxidant substances from natural plants and vegetables which can occur dimerization in the solution. The interaction between morin and the TritonX-100 micelles are studied by electronic absorption, fluorescence emission, ATR-FTIR spectra, FF-TEM (Freeze-fracture TEM), and the ab initio quantum calculation. Some interesting results are found.

Morin can be solubilized in the TritonX-100 spherical micelle mainly in the form of the dimer and the hydrophobic force is the main driving force. The morphology of the micelle is changed from spherical to rock-like and the size of the single spherical micelle is increased with the solubilization of the morin. Morin cannot be located inside the TritonX-100 rod-like micelles because of the compact structure and limited solubilization space of the rod-like micelles, but morin can exist in the form of the monomer and link the rod-like micelle by forming H-bonding with TritonX-100 to form a kind of network structure. The ab initio quantum chemical calculations of morin show that the stable structure of morin is not planar with the phenyl (B-ring) connected to the C-ring by a single C-C bond around which rotation can occur, and the B-ring deviates with 38.98° from the planarity. No matter morin interacts with TritonX-100 micelle in the form of monomer or dimer, the active site involves in the

interaction is always the phenyl group in the molecule, which leads to the limitation of the rotation of B-ring and the increased planarity of the whole morin molecule. The structure of morin dimer is determined by the nanoscale solubilization space of the spherical TritonX-100 micelle. The two B-rings (deviating with 38.98° from the planarity of the morin molecule) are linked by the H-bonding in a face to face mode making the two morin molecules pile up into dimer and the two piled up phenyls are whole located in the TritonX-100 spherical micelle.

12) Rheology and Dynamics of Complex Fluids

P12-01

Evaluating the Intrinsic Bending Force in Chiral Bilayer Membranes by Molecular Dynamics Simulations

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Bilayer membranes made of certain lipids can form twisted or helical ribbons as well as tubules with chiral molecular packing. According to a current continuum elasticity theory, such chiral supramolecular structures originate from an intrinsic bending force that appears in bilayer membranes with broken chiral symmetry. All variants of the continuum theory developed so far start by assuming a functional for the elastic energy of the bilayer membranes and end up expressing the optimal dimensions of the supramolecular structures in terms of several elasticity moduli. On the example of two glucolipids, which form tubules and twisted ribbons, respectively, we show here that instead of being assumed the relevant functional and elasticity moduli can be derived by molecular dynamics simulations of model bilayer membranes with an all-atom force field like CHARMM. The results of the simulations support directly the concept of an intrinsic bending force in chiral bilayer membranes.

P12-02

Atomic Force Microscopy Studies of Langmuir-Blodgett Films: Phase Transitions in Phospholipid Monolayers

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Phase behavior and surface structure of dipalmitoyl phosphatidyl choline (DPPC) spread as Langmuir monolayers at the air/water interface in the absence and in the presence of two drugs in the aqueous phase, such as procaine (PR) or deferoxamine (DFO), at a drug concentration of 10^{-3} and 10^{-6} mole dm^{-3} , respectively, have been investigated using Langmuir-Blodgett (LB) technique and atomic force microscopy (AFM). The LB films were transferred on solid substrates, like glass optically polished and mica, at different controlled surface pressures by using vertical transfer and horizontal deposition method. Depending on the lateral surface pressure, highly ordered structures and less organized features have been

directly evidenced. In addition these observations reveal some specific molecular interactions between these biologically relevant biocompounds. The data also indicate that both procaine and deferoxamine can penetrate and interact with phospholipid monolayers stabilizing the membrane lipids at both internal and external membrane interfaces.

P12-03

The Rheology and Shear-Induced Microstructure of Nanoaggregate, Fumed Silica Dispersions

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The rheology of polymeric suspensions of fumed silica particles of varying volume fraction, sizes, and surface modifications are examined. Fumed silica particles are often described as aggregated, fractal-like structures. These fractal aggregate suspensions shear thicken at much lower particle loadings than suspensions of hard, spherical particles. For example, discontinuous shear thickening was observed for a suspension (fumed silica in polyethylene glycol) with a particle loading of only 7% by vol. In this work we explore the mechanism and underlying structure of fumed silica particle dispersions by rheology, microscopy, and light scattering. Thixotropy of the suspensions is also explored with rheological experiments. The results are compared to previous results for shear thickening in near hard sphere suspensions.

P12-04

Numerical Simulation of Particle-Surface Interaction in a Turbulent Channel Flow

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This study presents a computational model for Lagrangian simulation of particle transport, dispersion, and deposition including the possibility of rebound from the wall in a turbulent channel flow. An empirical mean velocity profile for the fluid velocity and experimental data for turbulent intensities are used in the analysis. The instantaneous fluctuating velocities are simulated by a continuous Gaussian random field model. The particle equation of motion takes into account the Stokes drag, the Saffman lift, the Brownian motion, and the gravitational forces. The Brownian diffusion is simulated as a white noise process. Starting with an initially uniform concentration near the wall, an ensemble of particle trajectories is generated and statistically analyzed. Several simulations for deposition of aerosol particles of various sizes are performed and the corresponding deposition velocities are evaluated. The computational model predictions for particle deposition velocity are compared with the existing experimental data and earlier simulation results and favorable agreements are observed.

P12-05

Gas-Liquid Dynamic Behavior in a Bubble Column Reactor

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Bubble coalescence and breakup-up are important processes that control the bubble size distribution in bubble column reactors. An experimental and computational study of the effect of gas superficial velocity on the bubble size distribution in a (200×10×1000 mm³) rectangular bubble column was performed. Bubble size distributions were measured using a high speed digital CCD camera and analyzed by LabVIEW image process system. Dispersed gas-liquid flow in bubble column was simulated by a population balance model Eulerian multiphase flow approach within the FLUENT code. The mechanisms of bubble breakup by the turbulence eddy and bubble coalescence were included in the analysis. It is seen that a central wave-like bubble plume appears with two staggered rows of vortices which control the roughly chaotic oscillation characteristics of the bubble column. The relations between the bubble size distributions in horizontal and vertical direction were studied. The model predictions were found to agree well with the experimental data.

P12-06

The Use of Spin-Echo NMR Experiments for the Investigation of the Dynamics in a Model Slurry System for CMP Containing Silica Particles

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With continuous increase in the complexity of current microelectronic devices and integration of Cu as interconnect, it is required that CMP provides a good surface planarity with minimal surface defectivity. One of the prominent roles of the abrasive particles is its ability to interact with chemical components found in the slurry. Surface adsorption of chemical components on to the abrasive particles can alter the intended chemical and mechanical balance of the slurry. Slurries consisting of abrasive particles of similar characteristics but different surface adsorption characteristic may perform differently in a CMP process. Furthermore, the introduction of copper ions during copper CMP may exacerbate the complexity. These copper ions could interact with the chemical components in the slurry to form copper complexes and also could change the adsorption characteristic of the abrasive particles. The formation of the copper complex and the change in the adsorption characteristic of the particles could have a great impact on the copper CMP performance. Performance will be exemplified with silica based slurry.

The longitudinal relaxation times (T_1) of the different components of CMP slurries were measured using Spin Echo-NMR (SE-NMR) at a constant temperature. The fact that NMR is non-invasive and gives information on the molecular level gives more advantage to the technique. The model CMP slurry was prepared in D₂O to enable monitoring of T_1 for the various components' protons. SE-NMR provide a very powerful tool to study the various interactions and adsorption processes that take place in a model CMP silica based slurry which contains BTA and/or glycine and/or Cu⁺² ions, it was found that BTA is very competitive towards complexation with Cu⁺² ions and BTA-Cu complex adsorbs on silica surface.

P12-06

Competitive surface adsorption of key chemicals on abrasive particles in copper CMP slurry

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Chemical mechanical planarization (CMP) is an enabling technology for the production of advanced semiconductor devices. It is used for producing global planar semiconductor wafer surface. One of the important constituent of CMP process is the CMP slurry. Slurry is a heterogeneous system consists of solid abrasive particles and reactive chemicals. Choosing appropriate slurry for the process will yield a better Cu CMP performance with less defects and high yield. To achieve this, it is important to understand the interactions among various components in the slurry. One of the prominent roles of the abrasive particles is its ability to interact with key chemical components found in the slurry due to its high surface area. During the CMP process the chemical components in the slurry undergo surface adsorption onto the abrasive particles. Surface adsorption of chemical components on to the abrasive particles can alter the intended chemical and mechanical balance of the slurry. It is equally critical to realize that such a surface adsorption characteristic is unique to each type of particles and the chemical profile of the surface. Slurries consisting of abrasive particles of similar characteristics but different surface adsorption characteristic perform differently in a CMP process. The difference in the surface adsorption characteristic between the abrasive particles results in variation in the interaction between the particles and the chemical constituent in the slurry.

In this talk, competitive surface adsorption of key chemicals on abrasive particles in copper CMP slurry will be discussed. The experimental techniques used in this study will be described. Some potential implications and applications will be discussed.

P12-07

A New Passivating System for Copper CMP

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In today's slurry for Chemical Mechanical Polishing (CMP) of copper interconnect during wafer processing for advanced microelectronic manufacturing, the commonly used passivating mechanism is based on the formation of a thin layer of water insoluble copper complex. The low solubility of such a complex film prevents the dissolution of copper which protects the lower lying area from chemical attack. One of the most commonly used compounds for such a purpose is benzotriazole (BTA). Although BTA has been widely used in commercially available CMP slurries and other corrosion prevention formulations, it also yielded many challenges such as post CMP clean, over sized particle formation during CMP, and batch to batch consistency.

This poster presents a study in which an alternative mechanism for passivating metal surface is suggested. More specifically, a surfactant system was used to replace molecules such as

BTA to form an adsorption layer on the surface of copper. It is found that the strength of the passivation effect is a function of pH, surfactant structure, surfactant concentration, and counter ions.

In this poster presentation, some background information on CMP slurry requirement and working principles will be first introduced. A set of comparative experimental results based on BTA and a surfactant system will be described. The feasibility of using such a surfactant system for copper CMP slurry formulation, especially in the acidic region such as pH = 5, will be analyzed. An even broader implication of using such a concept in other anti-corrosion applications will be further speculated.

13) Role of Phase Science in Colloid and Surface Science

P13-01

Investigations of Emulsion Films using Electrochemical Methodology.

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A new method for studying properties of thin liquid emulsion films has been developed. The Exerowa-Scheludko thin liquid film cell was modified by inserting a pair of electrodes into the water containing compartments. DC voltage applied across the film allowed measurements of a critical voltage at which the film breaks. A small AC signal was used to measure the film capacitance. Measurements were conducted for water – Athabasca bitumen diluted with 50:50 mixture of heptane and toluene. The measured changes in the film capacitance can be due to film thinning and/or changes in the film structure or composition. Build-up of the surface layer that stabilizes water-in-crude oil emulsions is a slow process taking at least minutes if not hours. The dependence of the initial rate of change in the film capacitance with time on bitumen concentration indicates that surface composition at low concentrations is markedly different from that at high bitumen concentrations.

P13-02

Stratification and “Stained Glass” Behaviour in Foam Films from Complex Aerosol-OT Solutions.

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Stratification of foam films drawn from aqueous Aerosol-OT solutions at concentrations well below lamellar liquid crystal (LLC) phase boundary is due to layers of ordered micelles. However, at higher concentrations, where LLC coexists with normal micellar solution in bulk, film stratification is due to stacked bilayers of surfactant molecules. The distance between the ordered bilayers, i.e., d-spacing, in the film is smaller than that for the bulk LLC phase. As the Aerosol-OT concentration increases, the thickness at which the first stratification step occurs increases and the final equilibrium film thickness decreases. Contrary to popular believe the first stratification step can occur well above 60-70 nm. Indeed, for films showing LLC-like

structure, film stratification was observed in films several micrometers thick. Here, the film is composed of a number of domains of uniform color (thus of uniform thickness) with sharp boundaries, resembling 'stained glass'. Those thick domains may coexist with black film domains, 18 nm thick, in a single film specimen.

P13-03

Capillary Forces between Surfaces in a Liquid Crystal near its Isotropic-to-Nematic Phase Transition Temperature

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The interaction forces between the particle and plate in 8CB liquid crystal near its isotropic-to-nematic transition temperature have been measured in-situ using an atomic force microscope (AFM) with temperature controllers. As a result, we found that 8CB molecules orient perpendicular to the DMOAP-coated glass surfaces (i.e., homeotropic orientation), whereas they orient parallel to the graphite and the carbon surfaces (i.e., homogeneous orientation). When two surfaces were of the same kind, attractive forces were observed between them. These attractive forces are attributed to the confinement-induced phase separation of the liquid crystal. On the other hand, only repulsive forces were observed between two surfaces of the different kind.

P13-04

An ATR-FTIR Study of Dicarboxylic Acids at the Hematite/Water Interface

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The focus of the present study is on a molecular-level understanding of the bonding mode and structure of simple carboxylic acids at the hematite/water interface. We present results for four simple dicarboxylic acids (phthalic, maleic, fumaric, succinic acid) and investigate how surface complex structures and modes are affected by small differences in the molecular structures of the organic acids. Applying attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy and batch adsorption experiments, we characterized the adsorption of these organic acids to hematite as a function of pH, ionic strength, and surface loading. Our macroscopic results show that the pH for maximum adsorption is closely related to the pK_{a2} of these organic acids. In the circum-neutral pH range the highest adsorption density is found for phthalic acid and maleic acid, followed by succinic acid. Fumaric acid shows the weakest adsorption. The IR spectra for adsorbed acids are similar to the spectra for phthalate, maleate, fumarate, and succinate ion in solution, exhibiting only small variations with pH, ionic strength, and surface loading. We interpret these IR results to indicate the presence of single dominant fully deprotonated outer-sphere complex (i.e., $FeOH_2^+X^{2-}$) for all of the dicarboxylic acids in the study.

P13-05

IR-Raman Investigation of the Structure and Energy Transfer Dynamics of a Reverse Micelle Surfactant Layer

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IR-Raman spectroscopy is used to analyze the structure and energy transfer dynamics of a reverse micelle surfactant layer. This technique uses a femtosecond infrared laser pulse to excite a specific vibrational motion in the system while subsequently monitoring the anti-Stokes Raman signal with a second laser pulse at varied delay times. The movement of vibrational energy in the system can then be determined by analyzing the changes in the Raman signal. Also, the emulsions used in this experiment were formulated such that each structural domain of the system gave a unique response in the vibrational spectrum of the system allowing for a correlation between spectral and spatial resolution. Both the rate and mechanism of vibrational energy transfer across the interfacial region were then measured. The rate of vibrational energy transfer to the nonpolar continuum is shown to be dependent on where the energy was deposited into the system.

14) Microelectronic and Photonic Applications

P14-01

New Liquid Mirrors from Silver Nanoparticles: Optimization of Reflectivity by Controlling Nanoparticle Size

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We have been investigating thin reflective surface films of silver nanoparticles at the air-water interface. Such films represent a new class of liquid mirrors that constitute an excellent alternative to mercury mirrors because of their low density and low toxicity. The optical properties of the surface films clearly depend on certain characteristics of the silver nanoparticles employed in their fabrication. In particular, we have demonstrated that reflectivity depends on the size and shape of the constituent particles. Larger nanoparticles (80-120 nm) form better liquid mirrors than do smaller nanoparticles (20-50 nm). For this reason we have investigated the influence on particle size of various experimental parameters related to the preparation of the silver colloid. The suspensions of silver nanoparticles are prepared by the citrate reduction of silver nitrate (AgNO_3) in aqueous solution. The concentrations of both silver and citrate ion are found to influence nanoparticle size in an important way. The exact way in which citrate is introduced (all at once or stepwise) also has an important effect on nanoparticle formation. Finally, preliminary results involving the use of small silver particles as precursor seeds suggest that this procedure has much promise for the control of particle size through the number of germs introduced. The particles are characterized by transmission electron microscopy. The optical properties of the surface films are determined with a UV-visible spectrophotometer equipped with a reflectivity accessory. Future work will include experiments to establish the relationship between nanoparticle size and surface film thickness.

P14-02

Nanoparticles of Conjugated Polymer and Well-Organized Nanoporous TiO₂ Shell

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Synthesis of conjugated polymer-TiO₂ nanocomposites has been attracted for their useful applications in optoelectronic devices, such as solar cells, electrochromic devices, light-emitting diodes, and charge-storage devices, which make a heterojunction between organic and inorganic semiconductors where charge transfer occurs. A conjugated polymer-TiO₂ core-shell nanocomposite could be obtained by synthesizing polymethineimine and nanoporous TiO₂ shell simultaneously. Polymethineimine was synthesized by the ring opening polymerization of s-triazine as a complex with metal halide, such as ZnCl₂, SnCl₄, and TiCl₄. In addition, an ordered array of nanoporous TiO₂ was synthesized with frameworks of supramolecular assemblies. Recently, highly organized nanoporous TiO₂ was prepared by hydrolysis of TiCl₄ in the presence of surfactants or amphiphilic block copolymers. In this study, the core-shell nanoparticles of polymethineimine-nanoporous TiO₂ were synthesized within a short time by adding s-triazine to the mother solution of nanoporous TiO₂. The mixture of two triblock copolymers was used as a template material for nanoporous inorganic shell, and TiCl₄ was used as a catalyst for the ring-opening polymerization of polymethineimine and as a precursor of TiO₂.

P14-03

Synthesis and Characterization of Polymer Encapsulated Nanoparticles for Microelectronic Applications

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There are two well-researched methods for constructing the core-shell morphology of particles. The shell can be produced by adsorption of preformed macromolecules onto core surfaces by electrostatic or by non-solvent deposition methods. An alternate method involves mixing core particles with monomers and then initiating polymerization. This procedure is more favorable for obtaining a uniform coating of each particle because of the substantially higher accessibility of the active surface of cores for molecules of a monomer compared to the corresponding macromolecules. However, the formation of an organic shell on extremely small silica nanoparticles (~ 20 nm) by the same method has received little attention. In the present work; we demonstrate a process of coating of such small colloidal silica particles with polymers in two layers; the first layer is PDVB (polydivinylbenzene) and the second layer is PHEMA (poly2-hydroxyethylmetha-crylate). Results of several time based adsorption experiments are presented to verify the hypothesis of monomer adsorption on inorganic core with and without initiator. The presence of polymer encapsulating the silica surface was determined by FTIR spectroscopy, transmission electron microscopy (TEM) and ALV particle sizing instruments; while the amount of coated polymer on silica surface was assessed by thermogravimetric analysis (TGA). These polymer coated particles can be used as soft abrasives in CMP application to minimize defects.

15) Synthesis, Characterization and Applications of Bioinspired Nanomaterials

P15-01

Formation and properties of polysaccharide-based polyelectrolyte complexes

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So far the formation of polyelectrolyte complexes has been mainly studied for synthetic polyelectrolytes. Here we describe the complexation between two charged polysaccharides, polycationic chitosan and negatively charged hyaluronic acid. Dynamic light scattering shows that upon mixing these two polymers form submicrometer particles with the hydrodynamic radius depending on polymer concentration, molar ratio as well as molecular weight of two complexing polyelectrolytes. Chain length of chitosan is the major parameter affecting the dimensions of the complexes, i.e. an increase in the molecular weight of chitosan results in the formation of larger particles. The complexes were additionally characterized by atomic force microscopy, which shows the granular morphology and the size similar to that determined from light scattering data. Finally, the thermodynamics of interaction between chitosan and hyaluronic acid was studied using isothermal titration calorimetry.

P15-02

Enzymatic Synthesis of a Skin Scaffold

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The objective of skin substitutes is to restore the anatomy and the function of the normal skin after healing of the wound. Artificial skin grafts heal with extensive scarring and loss of some of the skin functions.

We are developing a polymeric scaffold based on a cross-linked polysaccharide. Horse Radish Peroxidase is being used as a catalyst in the synthesis. All the materials synthesized are based on the Poly(glucuronic acid). Several copolymers and cross-linked polymers will be presented. Degradation studies of the polymers and the surface characterization will also be included in the presentation.